

# PATENT SPECIFICATION

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## (54) CONTINUOUS PROCESS FOR THE PRODUCTION OF POLYURETHANES IN A FINELY DISPERSED FORM

(71) We, BAYER AKTIENGESELLSCHAFT of 509 Leverkusen, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

From German Offenlegungsschrift No. 1,645,656, it is known to produce stable aqueous polyurethane dispersions by mixing a polyurethane polymer which contains isocyanate end groups with water, cooling the mixture to between -5°C and 20°C and adding a chain-lengthening agent with stirring. In this process, the prepolymer must first be emulsified and then subjected to the chain-lengthening reaction in the emulsified state. Apart from requiring the preparation of a stable prepolymer emulsion, which remains stable during the chain-lengthening reaction, this process cannot be carried out continuously and the particle size of the dispersion obtained cannot be controlled. It is an object of the present invention to provide a continuous process for the production of polyurethane ureas in a disperse form. The process operates with very high volume/time yields, is simple to carry out and can be used for producing dispersions with any desired degree of fineness.

The process according to the invention generally comprises introducing an isocyanate prepolymer, a liquid aqueous phase and, optionally, a chain lengthening agent other than water continuously into a zone of high turbulence consisting of a space through which at least 300 parts by volume of liquid are passed per unit volume of space and per hour under conditions of vigorous mixing corresponding to a specific mixing power of from 5 to 25 Watt/cm<sup>2</sup> at a temperature above the melting point and below the decomposition point of the isocyanate prepolymer and of the chain-lengthening agent, effecting the iso-

cyanate polyaddition to produce polyurethane urea and the formation of a dispersion in this zone, continuously removing the polyurethane urea dispersion in the aqueous phase from this zone of high turbulence and optionally isolating the solid polyurethane ureas in the form of fine particles from this dispersion.

The three components may be introduced simultaneously but separately into the zone of turbulence, or the chain-lengthening agent may be mixed in a first step with the aqueous phase, and the mixture may be introduced with the prepolymer into the zone of turbulence. Within the meaning of this invention, isocyanate prepolymers are the reaction products of diisocyanates or polyisocyanates with compounds which contain at least two active hydrogen atoms and preferably have a molecular weight of from 400 to 10,000 and contain at least two isocyanate groups per molecule. This means that at least two mols of isocyanate groups must be present per mol of active hydrogen in the reaction.

Such isocyanate prepolymers are already known. They are generally prepared by reacting polyols of the appropriate molecular weight with diisocyanates of polyisocyanates.

Particularly suitable polyols for this reaction have a molecular weight of 400 to 10,000, preferably 1000 to 10,000, and contain from 2 to 8 hydroxyl groups per molecule. The polyols preferably used are polyesters, polyethers, polythioethers, polyacetals, polycarbonates and polyester amides. Suitable polyesters are, for example, the reaction products of polyhydric alcohols, preferably dihydric alcohols to which trihydric alcohols may be added, with polybasic, preferably dibasic carboxylic acids. Instead of the free polycarboxylic acids, the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or mixtures thereof may be used for producing the polyesters. The polycarboxylic acids may

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be aliphatic, cycloaliphatic, aromatic and/or heterocyclic and may be substituted, e.g. with halogen atoms, and/or unsaturated.

The following are mentioned as examples:

5 succinic acid, adipic acid, suberic acid, azelaic acid, sebatic acid, phthalic acid, isophthalic acid, trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, endomethylene tetrahydrophthalic acid anhydride, glutaric acid anhydride, maleic acid, maleic acid anhydride, fumaric acid, dimeric and trimeric fatty acids such as oleic acid, which may be mixed with monomeric fatty acids, dimethyl terephthalate and bis-glycol terephthalate. The following are examples of suitable polyhydric alcohols: ethylene glycol, propylene-1,2- and -1,3-glycol, butylene-1,4- and -2,3-glycol, hexane-1,6-diol, octane-1,8-diol, neopentyl glycol, cyclohexane dimethanol (1,4-bis-hydroxymethyl cyclohexane), 2-methylpropane-1,3-diol, glycerol, trimethylol-propane, hexane-1,2,6-triol, butane-1,2,4-triol, trimethylol-ethane, pentaerythritol, quinitol, mannitol and sorbitol, methyl glycoside, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycols, dibutylene glycol and polybutylene glycols. The polyesters may contain a proportion of terminal carboxyl groups. Polyesters of lactones such as  $\epsilon$ -caprolactone or hydroxycarboxylic acids such as  $\omega$ -hydroxy-caproic acid may also be used.

10 Suitable polyethers containing 2 to 8 and preferably 2 or 3 hydroxyl groups may be prepared, for example, by polymerising epoxides such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin, each with itself, e.g. in the presence of boron trifluoride, or by the addition of these epoxides, which may be added as mixtures or successively, to starting components which contain reactive hydrogen atoms such as alcohols or amines, e.g. water, ethylene glycol, propylene-1,3- or -1,2-glycol, trimethylolpropane, 4,4'-dihydroxydiphenyl-propane, aniline, ammonia, ethanamine or ethylenediamine. Sucrose polyethers such as those described e.g. in German Auslegeschriften No. 1,176,358 and 1,064,938 may also be used for the process according to the invention. It is frequently preferred to use polyethers in which the hydroxyl groups are predominantly primary hydroxyl groups (up to 90% by weight, based on all the hydroxyl groups present in the polyether). Polyethers which are modified with vinyl polymers such as those which can be obtained e.g. by the polymerisation of styrene or acrylonitrile in the presence of polyethers (US Patents No. 3,383,351; 3,304,273; 3,523,093 and 3,110,695 and German Patent No. 1,152,536) and polybutadienes which contain hydroxyl groups are also suitable.

15 Polythioethers which should be particularly mentioned are the condensation products of thiodiglycol with itself and/or with other glycols, dicarboxylic acids, formaldehyde, aminocarboxylic acids or amino alcohols. Depending on the co-component, the products obtained are polythio mixed ethers, polythioether esters or polythioether ester amides.

20 Suitable polyacetals are, for example, the compounds which can be prepared from glycols such as diethylene glycol, triethylene glycol, 4,4' - dihydroxyethoxy - diphenyl - dimethylmethane, hexanediol and formaldehyde. Suitable polyacetals for the process according to the invention may also be prepared by polymerising cyclic acetals.

25 The polycarbonates which hydroxyl groups may be those known *per se*, e.g. those which can be prepared by reacting diols such as propane-1,3-diol, butane-1,4-diol and/or hexane-1,6-diol, diethylene glycol, triethylene glycol or tetraethylene glycol with diaryl carbonates such as diphenyl carbonate or phosgene. The polyester amides and polyamides include, e.g. the predominantly linear condensates obtained from polybasic saturated and unsaturated carboxylic acids or their anhydrides and polyvalent saturated and unsaturated amino alcohols, diamines, polyamines and their mixtures.

30 Polyhydroxyl compounds which already contain urethane or urea groups and natural polyols which may or may not be modified, such as castor oil, carbohydrates or starch may also be used. Addition products of alkylene oxides with phenol-formaldehyde resins or urea-formaldehyde resins are also suitable for the purpose of the invention.

35 Representatives of these types of compounds which may be used according to the invention have been described e.g. in High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology" by Saunders-Frisch, Interscience Publishers, New York, London, Volume I, 1962, pages 32-42 and pages 44-45 and Volume II, 1964, pages 5-6 and 198 and 199 and in Kunststoff-Handbuch, Volume VII, Vieweg-Höchtl, Carl-Hanser Verlag Munich, 1966, e.g. on pages 45-71.

40 The diisocyanates or polyisocyanates used for converting the polyols into prepolymers which contain isocyanate groups may be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic polyisocyanates (see Ann. 562, pages 75-136), for example ethylene di-isocyanate, tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate, dodecane-1,12-diisocyanate, cyclobutane-1,3-diisocyanate and any mixtures of these isomers; 1 - isocyanato - 3,3,5 - trimethyl - 5 - isocyanatomethyl cyclohexane (German Auslegeschrift No. 1,202,785); Hexahydrotolylene-2,4- and -2,6-diisocyanate and any mixtures of these isomers; hexahydrophenylene-1,3- and/or -1,4-diisocyanate; perhydrophenylene-

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2,4- and/or -4,4'-diisocyanate; phenylene-1,3- and -1,4-diisocyanate; tolylene-2,4- and -2,6-diisocyanate and any mixtures of these isomers; diphenylmethane-2,4'- and/or -4,4'-diisocyanate; naphthylene-1,5-diisocyanate; triphenylmethane - 4',4"- triisocyanate; polyphenyl - polymethylene - polyisocyanates (obtained by aniline-formaldehyde condensation followed by phosgenation in accordance with British Patent No. 874,430 and 848,671); perchlorinated aryl polyisocyanates (see German Auslegeschrift No. 1,157,601); polyisocyanates which contain carbodiimide groups (see German Patent No. 1,092,007); the diisocyanates according to US Patent No. 3,492,330; polyisocyanates which contain allophanate groups (see British Patent No. 994,890; Belgian Patent No. 761,626 and Dutch Patent Application No. 7,102,524); polyisocyanates which contain isocyanurate groups (see German Patents Nos. 1,022,789; 1,222,067 and 1,027,394; German Offenlegungsschriften No. 1,929,034 and 2,004,048); polyisocyanates which contain urethane groups (see Belgian Patent No. 752,261 and US Patent No. 3,394,164); polyisocyanates which contain acylated urea groups (see German Patent No. 1,230,778); polyisocyanates which contain biuret groups (see German Patent No. 1,101,394; British Patent No. 889,050 and French Patent No. 7,017,514); polyisocyanates prepared by telomerization reactions (see Belgian Patent No. 723,640); polyisocyanates which contain ester groups (see British Patent No. 956,474 and 1,072,956; US Patent No. 3,567,763 and German Patent No. 1,231,688) and reaction products of the above mentioned isocyanates with acetals (see German Patent Specification No. 1,072,385).

The preparation of prepolymers which contain isocyanate groups from polyols and isocyanates is already known (see R. Vieweg, A. Höchtl, Kunststoff-Hanbuch, Volume VII, Polyurethane, Carl-Hanser-Verlag Munich, 1966, pages 84—85). Chain-lengthening agents for isocyanate prepolymers are compounds which contain at least two Zerewitinow active hydrogen atoms per molecule and have a molecular weight of from 18 to 500. These compounds react with the isocyanate groups of the prepolymers and build up high-molecular weight polyurethanes or polyurethane ureas by linking several isocyanate prepolymer molecules together. The chain-lengthening reaction is also already known. Among the known chain-lengthening agents, the following are particularly suitable: water, amino alcohols which contain hydroxyl and amino groups, aminosulphonic acids and aliphatic, cycloaliphatic or aromatic amines including hydrazine. The following are specific examples of such chain-lengthening agents: water, hydrazine, ethylenediamine, propylene-1,2-diamine, propylene-1,3-diamine, tetramethylenediamine, hexamethylenediamine, diethanolamine, diisopropanolamine, N,N'-bis-(3-aminopropyl) ethylenediamine, N,N'-bis-(2-aminopropyl)-ethylenediamine, N,N'-bis-(2 - amino - ethyl) - ethylenediamine, 4,4'-dimethylamino-diphenylmethane, 4,4'-dimino-3,3'-dimethyl-diphenylmethane, 4,4'-diamino-diphenylmethane, 2,4- and 2,6-diaminotoluene and taurine. The molar quantity of chain-lengthening agents used generally corresponds to the number of isocyanate groups present. The molar ratio of NCO:  $(H)_K$  is preferably 1 ( $[H]_K$  = active hydrogen in the chain-lengthening agent) although smaller quantities of chain-lengthening agents may be used (NCO:  $[H]_K$  1) down to about a ratio of NCO:  $[H]_K$  = 1.8, preferably down to 1.5. The molecular weight of the polyurethanes or polyurethane ureas will in that case be lower and their melting point also lower.

The aqueous phases used are preferably water or aqueous emulsifier solutions. The emulsifiers are generally used in quantities of 0.1 to 1% by weight based on the weight of the aqueous phase. The quantity of aqueous phase, based on the isocyanate prepolymer is preferably 50 to 80% by weight.

So-called laminators (see Belgian Patent Specification No. 718,029) may also be used either together with or instead of the emulsifiers.

The reaction is preferably carried out at a temperature at which all the reactants are liquid but it should not be higher than the decomposition temperature of the starting materials and of the polyurethane or polyurethane urea formed by the reaction. It is generally necessary to operate under a certain excess pressure; the pressure should at least be above the vapour pressure of the volatile components. The process is preferably carried out at a temperature of from 50 to 150°C. In the zone of high turbulence, the temperature should in any case be above the melting point of the isocyanate prepolymer because products will only then be obtained in the form of uniform spherical particles.

The zone of high turbulence generally means, in the context of this invention, a space through which at least 300 parts by volume of liquid are passed per unit volume of space and per hour under conditions of vigorous mixing. The volume of liquid passed through the zone of turbulence per unit volume turbulent zone and per hour is preferably 1200 and 5400 parts by volume. The time of stay of the mixture in the zone of turbulence is then between 6 seconds and less than 1 second.

The zone of high turbulence is generally produced by means of known apparatus, for example a stirrer vessel with disc stirrers and flow breakers may be used with a ratio of vessel diameter to stirrer diameter of between 1:0.9 and 1:0.2. When this apparatus is used, the various reactants may be supplied separately by introducing one component (e.g.

the aqueous phase plus chain-lengthening agent) directly into the stirrer cone and the other component (e.g. the isocyanate prepolymer) into the hollow shaft of the stirrer so that the two components are first emulsified and chain-lengthening then takes place in the already emulsified product.

Pumps equipped with rotors are particularly suitable for carrying out the process, mainly because the time of stay is strictly limited. Exceptionally vigorous mixing can be achieved within very short times of stay in rotary homogenization machines. These apparatuses are therefore preferred. They have a very high rate of throughput. The specific mixing power of rotary homogenization machines is about 5-25 Watt/cm<sup>3</sup>.

The process may be carried out by introducing all three components simultaneously but separately into the zone of turbulence or two of the components, e.g. the aqueous phase and the chain-lengthening agent, may be mixed. This is particularly advisable if the chain-lengthening agent is water-soluble. Alternatively, the reactants may be introduced at various points into the zone of turbulence and if desired, the stream of one component may be sub-divided into several partial streams, for example the prepolymer and aqueous phase may be introduced at the beginning of the zone of turbulence and the chain-lengthening agent may be introduced at several points simultaneously, at the beginning, the middle and/or the end of the zone of turbulence. According to one particularly advantageous method of carrying out the process, the reaction mixture is passed through a zone of decreasing temperature.

Since the chain-lengthening reaction takes place rapidly at high temperatures, it is advisable to employ high temperatures in the zone of turbulence. In order to operate the reaction continuously at its optimum conversion rate and, for example, to vary the particle size of the product, the zone of turbulence may be associated with additional zones of turbulence operated at decreasing temperatures. For example, the first zone of turbulence may be kept at a temperature above the melting point of the starting materials and of the polyurethane produced while a following reaction zone may be kept at a temperature near the melting point of the polyurethane and of the prepolymer while a following cooling zone may be kept at a temperature below the softening temperature of the polyurethane or polyurethane urea. The polyaddition reaction may be stopped by washing the reaction mixture with acidified water. The process according to the invention will now be described in more detail with reference to the accompanying drawings. Figure 1 shows an arrangement apparatus (1) is continuously supplied with an isocyanate prepolymer from the storage tanks (10) by way of the gear wheel pump (11) and the valve (12) and at the same time with emulsifier and chain-lengthening agent by way of piston delivery pumps (6 and 7), valves (5), mixing device (4), heat exchanger (3) and non-return valve (2). The isocyanate prepolymer is emulsified in the mixing apparatus (1), the prepolymer forming the disperse phase of the emulsion. The chain-lengthening reaction of the prepolymer is also carried out in this apparatus by the simultaneous addition of the chain-lengthening agent. After the preparation of the emulsion in the mixing apparatus (1), the emulsion is transferred to the reaction vessel (14) by way of a pressure control valve (13) and a pH-meter (15). The reaction is completed in this reaction vessel (14).

The chain-lengthening agent may also be introduced directly into the mixing apparatus (1) by way of the pump (7a) and non-return valve (2a) or it may be introduced behind the mixing apparatus by way of the pump (7b) and the valve (2b). If desired, part of the chain-lengthening agent may be introduced along one path and part along the other. The pH is the governing parameter used to determine the manner in which the reaction is controlled.

Figure 2 shows another apparatus for carrying out the process. In this case, a mixing apparatus (6) is supplied simultaneously with isocyanate prepolymer from an extruder (17), with the aqueous phase from the storage vessel (1) by way of a piston delivery pump (2), non-return valve (3) and heat exchanger (4) and with chain-lengthening agent from storage vessel (10) by way of piston delivery pump (8) and non-return valve (5). The emulsion produced in the mixing apparatus (6) enters the reaction tube of the heating circuit (9). Part of the emulsion is recirculated from this tube into the mixing apparatus (6) and the remainder is transferred to the reaction tube of the cooling circuit (15) through the reducing aperture (16). Part of the contents of this tube is passed through the cooler (12) and rotary pump (11) to be cooled in the cooling circuit and part is discharged into the tank (13). The whole plant is under the pressure of nitrogen which is introduced into the reaction tube (15) and tank (13) from the cylinder (14). The invention will now be further described with reference to the examples of the process carried out using an apparatus according to Figure 1.

#### Example 1.

Using a high-speed rotary homogenization apparatus with a capacity of 0.15 litres, a rotation of 6000 1/min and a specific mixing power of 23 Watt/cm<sup>3</sup>, an isocyanate prepolymer having a free isocyanate group content of 9% and based on adipic acid ethylene glycol polyester with a molecular weight of about 2,000, a polyester of adipic acid, hexane-

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1,6-diol and neopentyl glycol which has a molecular weight of about 17 and hexamethylene diisocyanate are continuously passed through the apparatus at the rate of 80 kg/h at a temperature of 100°C and, at the same time, an aqueous solution of emulsifier (0.2% styromalamine solution) is passed through at the rate of 300 litres per hour at 90°C. The two liquids enter directly into the mixing zone of the homogenization apparatus separately from each other. An emulsion is formed with the prepolymer forming the disperse phase. At the same time, a reaction between the isocyanate prepolymer and water takes place which is accompanied by chain-lengthening and urea formation. The volumetric rate of flow per hour is 2530-times the volume of the homogenization apparatus. The emulsion is transferred to a reaction vessel where it is kept at 90°C for 15 minutes with stirring and then cooled. The emulsion separates into a concentrated top layer and a serum and the resulting top layer which is 30—50% concentrated is highly thixotropic. After removal of the serum, the concentrate may be dried in shelf driers or flow driers to form a polyurethane powder. A very fine, easily flowing powder is obtained which has a particle size of 1—50  $\mu$  and a melting point of 180°C.

## Examples 3—18.

The method of procedure is the same as in Example 1 but the experimental conditions were varied and chain-lengthening was effected by adding ethylenediamine to the aqueous phase. The experimental conditions are indicated in Table 1.

TABLE I

Example No.	Isocyanate content of the prepolymer %	NH/NCO molar ratio	Isocyanate groups reacted with ethylene diamine %	Rate of throughput of prepolymer kg/h	Rate of throughput of aqueous phase kg/h	Temperature of prepolymer °C	Temperature of aqueous phase °C	pH of pH suspension	Sintering point of powder °C
3	1.15	1.0	1.15	80	300	100	90	9	78
4	1.7	2.0	1.7	80	300	100	90	10	72
5	2.0	1.0	2.0	68.4	270	100	90	8.7	105
6	2.4	0.9	2.16	81.6	340	100	90	7.8	113
7	2.88	0.25	0.72	54	300	100	90	6	60
8	2.88	0.5	1.14	55	300	100	90	5.5	63
9	2.88	0.75	2.16	54	300	100	90	8.5	104
10	2.88	0.90	2.59	87.6	340	100	90	8.15	150
11	2.88	1.0	2.88	55	300	100	90	8.5	153
12	2.88	1.1	2.88	88.2	300	100	90	9.0	159
13	2.88	2.0	2.88	80	300	100	90	9.5	158
14	6.22	0.25	1.55	80	300	100	90	6	81
15	6.22	0.5	3.11	92.5	340	100	90	6	165
16	6.22	0.75	4.66	92.4	340	100	90	7.6	174
17	6.22	1.00	6.22	92.4	340	100	90	8.0	175
18	6.22	1.10	6.22					9.0	179

## Example 19.

The experiment was carried out under the same conditions as in example 6 but half the chain-lengthening agent was introduced into the mixing zone of the homogenization apparatus and the other half was introduced into the reaction vessel only after emulsification. The powder obtained is finer than in example 6.

10 Examples using an apparatus according to Figure 2.

## Example 20.

Using a rotary homogenization apparatus with a speed of rotation of 6000 1/min, a mixing volume of 0.15 litre and a specific mixing power of 23 Watt/cm<sup>3</sup>, a polyurethane prepolymer containing 2% of free isocyanate groups and based on an adipic acid/ethylene glycol polyester having a molecular weight of about 2000, a polyester of adipic acid, hexane-1,6-diol and neopentyl glycol having a molecular weight of about 1700 and hexamethylene diisocyanate are continuously introduced into the beginning of the zone of turbulence of the homogenisation apparatus at the rate of 19 kg per hour and at a temperature of 120°C and at the same time an aqueous solution of emulsifier (0.2 % aqueous styromalamine solution) is also continuously introduced there at a rate of 40 kg per hour and at a temperature of 100°C. A 10% aqueous solution of ethylenediamine used as chain-lengthening agent is added separately at the end of the zone of turbulence of the homogenization apparatus at the rate of 1.43 kg per hour. The emulsion formed in the homogenization apparatus enters the reaction tube at 120°C. In this reaction tube, the chain-lengthening reaction is completed and the irregular oval or fibrous particles formed in the homogenization apparatus are converted into spherical particles. After passing through the reaction tube, part of the emulsion is recirculated in to the emulsification apparatus by the pumping action of the homogenization machine. This enables the concentration of the emulsion to be adjusted independently of the relative output rates of the delivery devices. At the same time, a pressure difference between the output end and input end of the rotary homogenization machine is avoided. A quantity of emulsion corresponding to the fresh quantities of reactants supplied is transferred to the cooling circuit through a reducing aperture and is cooled to 50°C in the reaction tube. Part of the suspension is kept in circulation to accelerate cooling. The excess pressure in the apparatus is adjusted to 3 bar with nitrogen so that the most volatile component will not boil and, if necessary, the pressure is regulated by discharging suspension from the pressure vessel through a valve. The resulting suspension is processed into a fine powder as in example 19. The sintering point of the powder is 105°C.

## Example 21.

The process was carried out under the conditions described in example 20 but only 1.1 kg per hour of 10% ethylenediamine was used. The NH/NCO molar ratio is 0.8. The powder obtained from a finely divided suspension has a sintering point of 95°C.

## WHAT WE CLAIM IS:—

1. A process for the continuous production of a disperse polyurethane urea in which an isocyanate prepolymer, a liquid aqueous phase and, optionally, a chain lengthening agent other than water are continuously introduced at a temperature above the melting point and below the decomposition point of the isocyanate prepolymer and of the chain-lengthening agent into a zone of high turbulence where isocyanate polyaddition to produce the polyurethane urea is carried out and a polyurethane urea dispersion in the aqueous phase is continuously removed from the zone of high turbulence consisting of a space through which at least 300 parts by volume of liquid are passed per unit volume of space and per hour under conditions of vigorous mixing corresponding to a specific mixing power of from 5 to 25 Watt/cm<sup>3</sup>, and a solid polyurethane urea may be isolated from this dispersion in the form of fine particles. 70
2. A process as claimed in claim 1 in which the three components are introduced simultaneously but separately into the zone of turbulence. 75
3. A process as claimed in claim 1 in which the chain-lengthening agent and the aqueous phase are mixed in a first step, which mixture is then introduced simultaneously with the prepolymer into the zone of turbulence. 80
4. A process as claimed in any of claims 1 to 3 in which the isocyanate prepolymer is the reaction product of a polyol with a diisocyanate or a polyisocyanate. 85
5. A process as claimed in claim 4 in which the polyol has a molecular weight of from 400 to 10,000. 90
6. A process as claimed in claim 5 in which the polyol has a molecular weight of from 1,000 to 10,000. 95
7. A process as claimed in any of claims 4 to 6 in which the polyol contains from 2 to 8 hydroxyl groups per molecule. 100
8. A process as claimed in any of claims 4 to 7 in which the polyol is a polyester, polyether, polythioether, polyacetal, polycarbonate or polyester amide. 105
9. A process as claimed in any of claims 4 to 8 in which the diisocyanate or polyisocyanate is an aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic diisocyanate or polyisocyanate. 110
10. A process as claimed in any of claims 1 to 9 in which the chain-lengthening agent is a compound which contains at least two active hydrogen atoms and which has a molecular weight of from 18 to 500. 115
11. A process as claimed in any of claims 1 to 10 in which the aqueous phase is an emulsion. 120
12. A process as claimed in any of claims 1 to 11 in which the isocyanate prepolymer is a prepolymer of a diisocyanate and a polyol. 125
13. A process as claimed in any of claims 1 to 12 in which the chain lengthening agent is a compound which contains at least two active hydrogen atoms and which has a molecular weight of from 18 to 500. 130

11. A process as claimed in claim 10 in which the molar ratio of isocyanate groups in the prepolymer to active hydrogen in the chain-lengthening agent is one.

12. A process as claimed in any of claims 1 to 11 in which the aqueous phase is water or an aqueous emulsifier solution.

13. A process as claimed in claim 12 in which the aqueous phase is an aqueous emulsifier solution which contains from 0.1 to 1% by weight of emulsifier.

14. A process as claimed in any of claims 1 to 13 in which the quantity of aqueous phase is between 50 and 80% by weight, based on the isocyanate prepolymer.

15. A process as claimed in any of claims 1 to 14 which is carried out at an excess pressure above the vapour pressure of the volatile components.

16. A process as claimed in any of claims 1 to 15 which is carried out at a temperature of from 50 to 150°C.

17. A process as claimed in any of claims 1 to 16 in which the zone of high turbulence is such that the volume of liquid passed through the zone of turbulence per unit volume

of turbulent zone per hour is between 1200 and 5400 parts by volume.

18. A process as claimed in any of claims 1 to 17 in which the isocyanate prepolymer and/or the chain-lengthening agent is supplied to the zone of high turbulence in several partial streams.

19. A process as claimed in any of claims 1 to 18 in which the polyaddition reaction is terminated by washing the reaction mixture with acidified water.

20. A process as claimed in claim 1 substantially as herein described with reference to any of the accompanying drawings.

21. A process as claimed in claim 1 substantially as herein described with reference to any of the Examples.

22. A disperse polyurethane urea when prepared by a process as claimed in any of claims 1 to 21.

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## COMPLETE SPECIFICATION

2 SHEETS

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Sheet 1

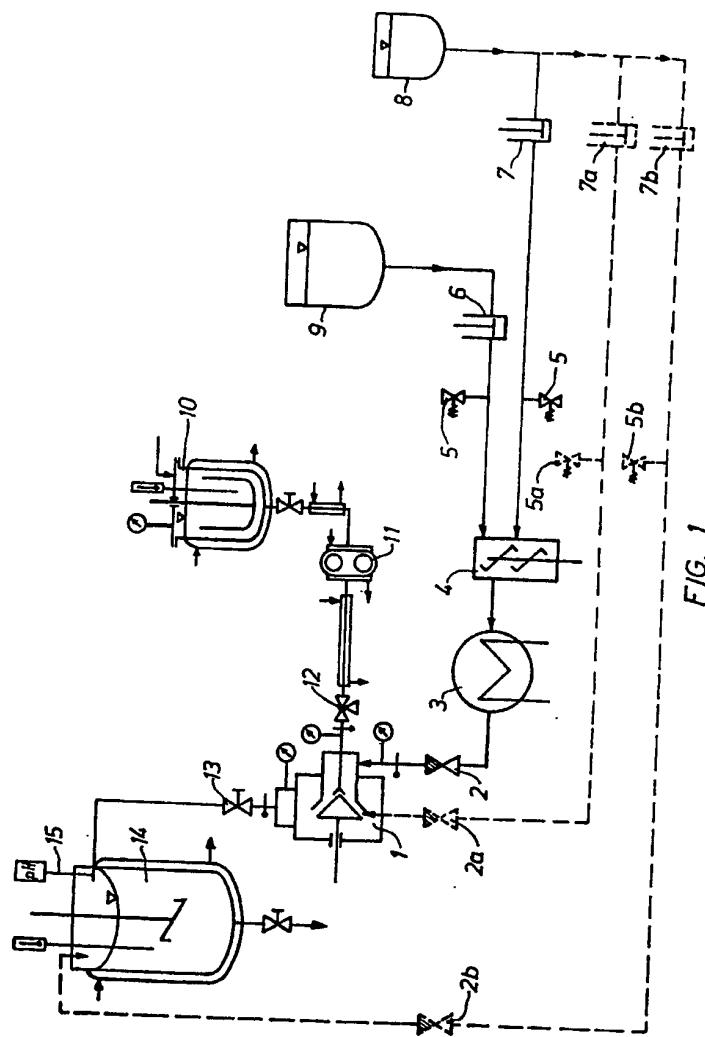


FIG. 1

